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Abstract

Studies of divinylbenzene copolymers and dimethacrylate homopolymers indicate that the polymer pore size controls the separation of water and ammonia on porous-layer-open-tubular (PLOT) columns. To a lesser degree, the polarity of the polymers also affects the separation of a water–ammonia gas mixture. Our results demonstrate that the pore size can be regulated by controlling the cross-linking density or the chain length between the cross-linking functional groups. An optimum pore size will provide the best separation of water and ammonia.

Introduction

Exobiology has been and continues to be a subject of interest to NASA. From our knowledge of life on Earth, we know that the presence of water and ammonia was of critical importance for chemical evolution and the origin of life. The examination of extraterrestrial bodies (in other words, planets, moons, comets, and planetary dust) for the presence of water, ammonia, and other biogenic compounds and elements is an object of much analytical effort. Gas chromatography (GC) can be used for the analysis of water and amines (1–3); however, columns that produce good separation are difficult to find. Although several liquid-coated columns have been reported (4,5) for this application, they cannot be used in conjunction with highly sensitive detectors such as the ion mobility spectrometer (IMS) or metastable ionization detector (MID) because of bleeding problems associated with these columns (6,7). For these reasons, NASA-Ames Research Center is involved in low or no-bleed column development for GC use.

Current commercial columns separate water–ammonia solutions through temperature programming. In flight missions, an isothermal condition is preferred. Under isothermal conditions, most of the commercial columns either cannot give good separation or have severe tailing problems. Recently, several porous-layer-open-tubular (PLOT) columns were developed and investigated in our laboratory for the separation of water–ammonia

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solutions (8). We describe the polymer pore size and solubility effects on water–ammonia separation.

Experimental

Materials. Divinylbenzene (DVB) (95% purity) (Dow Chemical; Midland, MO) and ethyleneglycoldimethacrylate (EGDM) (Arco Chemical Co.; Newton Square, PA), diethyleneglycoldimethacrylate (DEGDM), triethyleneglycoldimethacrylate (TEGDM), tetraethyleneglycoldimethacrylate (TTEGDM), polyethyleneglycol (400)dimethacrylate (PEGDM), 1,4-butanediol dimethacrylate (BTDM), 1,6-hexamethylene dimethacrylate (HMDM), pentaerythritol tetramethacrylate (PTMA), and pentaerythritol triacrylate (PTAA) (all from Polysciences, Inc.; Warrington, PA) were passed through a column of Supersorb 22 (Membrane & Polymer Technology; San Jose, CA) to remove the polymerization inhibitor before use. Styrene (Aldrich; Milwaukee, WI) was treated with 1M NaOH solution. The styrene layer was separated and dried with CaO before use. Methanol (J.T. Baker; Phillipsburg, NJ), isopropanol, heptane (Matheson Coleman & Bell; Cincinnati, OH), 2,2'-azobisisobutyronitrile (Polysciences), and methylethylketone (J.T. Baker) were used as received without purification.

Column preparation. Columns were prepared by the in situ polymerization method previously described (8). In each case, a solvent was selected from one of the following to produce the column: methanol, isopropanol, heptane, or mixtures of each.

Gas chromatographic evaluation. The column prepared from the in situ polymerization method was installed in a GC that was equipped with a thermal conductivity detector. Helium carrier gas was used to separate the various compounds. Gas samples were injected onto the column using a gas sample valve. The flow rate and operational temperature are given in the figures.

Scanning electron microscope evaluation. The scanning electron microscope (SEM) pictures (Figure 1) were taken by a Hitachi S-4000 Field Emission Scanning Electron Microscope. The samples were prepared by the following method: A portion of the column (1 in. length) was cut using a file; the samples were mounted on a plate; to prevent the samples from charging, the samples were sputtered for 3 min with gold using a Polaron E5100 SEM Coating Unit; finally, the samples were viewed and pictures were taken at 2.0 kV and magnifications of 7.00 K and 50.0 K, respectively.

Results and Discussion

Column preparation

The PLOT columns prepared by in situ polymerization can be classified into three types:

- Columns with very low operational pressure (less than 10 psi at 3–4 mL/min flow rate) that are formed when the particles are small but stable and the coating is uniform
- Columns with medium operational pressure (P) (50>P>10 psi) that are produced by formation of very small and unstable particles that coagulate and form large clusters thereby reducing the column passway
- Columns with high operational pressure (more than 50 psi) that are formed when small particles aggregate and completely block the column in many thin segments.

Figure 1A shows an HMDM PLOT column made using a butanol–hexane solvent system. The formation of properly sized latexes produces a very uniform coating. The operational pressure at a flow rate of 4–6 mL/min is only 10 psi. The column separation efficiency is also very high. Figure 1B shows an HMDM PLOT column produced using a heptane solvent system. Very small particles form at the beginning; later, aggregation occurs, and clusters form. Although it has high porosity, the column is plugged even at pressures over 100 psi. It is clear that selection of a suitable solvent system for polymerization is very important for producing PLOT columns with low operational pressures.

Water and ammonia separation

Porapak N, which is made from DVB–EGDM, has already been shown to separate water and ammonia (9,10). Therefore, different ratios of DVB–EGDM were used to produce in situ polymerized PLOT columns for this separation. The water–ammonia solution relative retention (r_{H_2O}/r_{NH_3}) can be calculated as follows:

$$V_{H_2O} / V_{NH_3} = (r_{H_2O}/r_{NH_3}) = (t_{H_2O} - t_{air}) / (t_{NH_3} - t_{air}) \quad \text{Eq 1}$$

where V_{H_2O} and V_{NH_3} are the specific retention volumes of water and ammonia, and t_{H_2O}, t_{NH_3}, and t_{air} are retention times of water, ammonia, and air, respectively. The water–ammonia relative retention increases with an increase in the concentration of EGDM as shown in Figure 2.

Two factors, pore size and solubility, are important in GC separation, adsorption, and desorption processes (11). Adsorption is related to the solubility factor, which is mainly determined by the ability of the gases to condense as well as the physical interaction of a gas molecule with the polymer matrix. Desorption is primarily determined by the size of a gas molecule as well as factors such as polymer segmental mobility and intersegmental packing density (or pore size).

To determine which factor influences the separation of water and ammonia in DVB–EGDM PLOT columns, we examined the solubility parameter first.

In recent years, gas–liquid chromatography (GLC) has been used to determine thermodynamic parameters for polymer substrates (12–14). Based on inverse chromatography, the solubility parameter can be estimated (15). It is clear that the retention volume of a substrate is related to the polymer-solvent (or Flory-Huggins) interaction parameter (16), x, as shown in the following equation:

$$x_{12} = \ln (273.15\, R\, v_{2sp} / Vg\, v_1\, P_1) - (1 - v_1/M_2 V_{2sp}) - (P_1/ RT)(B_{11} - v_1) \quad \text{Eq 2}$$

where M_2 is the number average molecular weight of the polymer, v_{2sp} is the specific volume of the polymer at the column temperature (T), Vg is retention volume from GC analysis, v_1 is the molar volume of the solvent, P_1 is the vapor pressure of the solvent at the column temperature, B_{11} is the gas-state second virial coefficient of the solvents, and R is the gas constant. Although this equation is only applied at the polymer melt state, the retention volumes should also relate to the interaction between gases and the cross-linking polymer. Based on the interaction parameter (x_{12}), the solubility parameter of the polymer and the solvent can be expressed by the following equation:

$$x_{12} = (v_1/r) (\gamma 1 - \gamma 2) \quad \text{Eq 3}$$

where γ_1 and γ_2 are the solubility parameters of the polymer and solvent, respectively.

Because the solubility parameters of DVB and EGDM are very close (9.28 and 9.5 [cal/cm^3]$^{1/2}$) as estimated by Fedors' method (17), the solubility parameters of their copolymers should be very close. Therefore, their water–ammonia separation factors should be similar. This is not observed (Figure 2).

In this case, the pore size may be the controlling factor. To test this hypothesis, DVB–styrene in situ polymerized PLOT columns were prepared. The solubility parameter for styrene is 9.3 (cal/cm^3)$^{1/2}$, which is very close to the DVB value. The relative retention of the water–ammonia solution also increases with increasing styrene concentration up to 43% (Figure 2).

To further confirm the pore size effect, PLOT columns prepared from homopolymers of DEGDM, TEGDM, TTEGDM, and PEGDM were tested. The results listed in Table I indicate that an increase in the chain length between the dimethacrylate func-
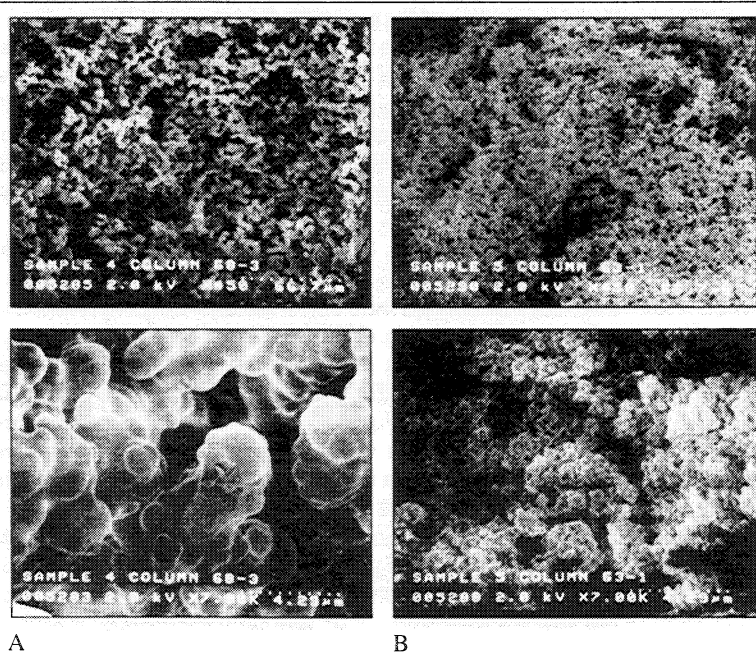

Figure 1. Scanning electron microscope photographs of 1,6-hexamethylenedimethacrylate (HMDM) polymer particles coated on the wall of the porous-layer-open-tubular (PLOT) columns prepared from in situ polymerization: A, butanol–hexane solvent system and B, heptane solvent system.
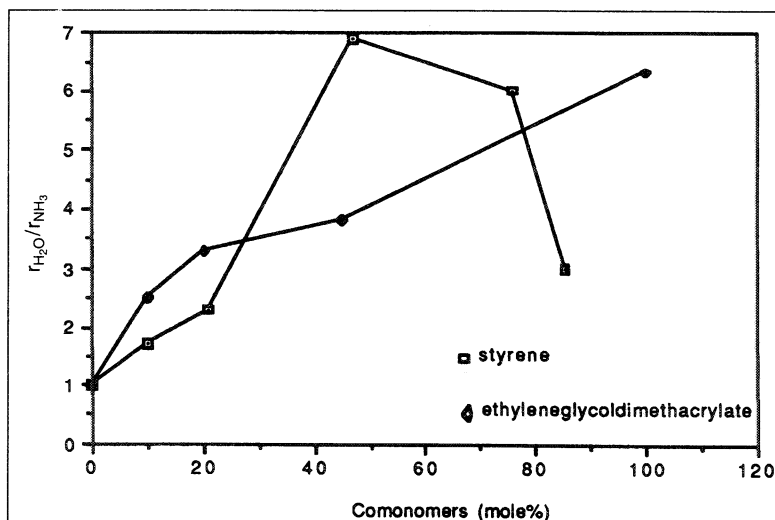
Figure 2. Effect of the mole percent of styrene and EGDM comonomers in divinylbenzene copolymer PLOT columns for water–ammonia solution separation.

Table I. Water–Ammonia Relative Retentions ($r_{H_2O} - r_{NH_3}$)

Column	Polymers*	$r_{H_2O} - r_{NH_3}$	Operational pressure†	Solvent system
50-1	EGDM	6.2	a	heptane–*t*-butanol–MEK
78-5	DEGDM	10.0	a	MEK–*t*-butanol
71-2	TEGDM	12.8	a	MEK–heptane
78-1	TTEGDM	18.1	b	MEK–*t*-butanol
56-3b	PEGDM	12.0	b	heptane–*t*-butanol–MEK
68-2	BTDM	8.0	a	MEK–methanol
68-3	HMDM	9.5	a	MEK–methanol
62-2	PTAA	1.1	b	heptane–*t*-butanol/MEK
78-2	PTMA	1.2	b	MEK–*t*-butanol
	Porapak N‡	4.7		

* See Appendix for abbreviations.
† Carrier gas pressure applied to obtain flow rate of 4 mL/min. a < 10 psi, 50 psi < b < 10 psi, and c > 50 psi.
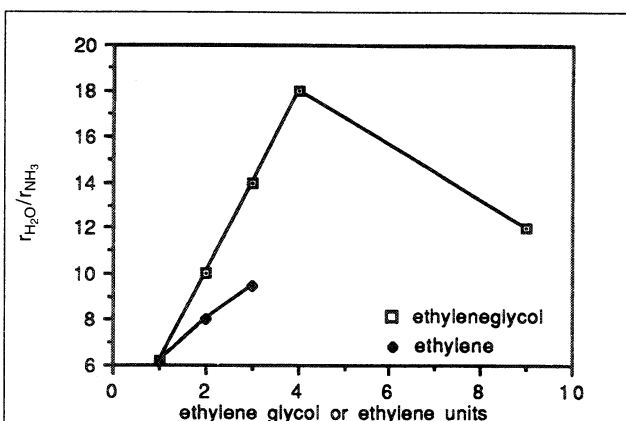‡ Alltech Chromatography, Deerfield, IL.

Figure 3. Effect of chain length between two methacryloyl groups in water–ammonia solution separation.

tional groups of the dimethacrylate homopolymer increases the separation between water and ammonia (Figure 3).

It is clear that cross-linking density may control the pore size; the higher the cross-linking density, the smaller the pore size produced. The multifunctional monomers, such as PTAA (which has a trifunctional double bond) or PTMA (which has a tetrafunctional double bond), form higher cross-linked and smaller pore-sized polymers; therefore, water and ammonia are not separated as completely (Table I).

When the styrene concentration is more than 43%, the relative retention of a water–ammonia solution decreases with increasing styrene concentration (Figure 2). A possible explanation for such behavior is that because styrene has nonfunctional double bonds, any increase above a 43% styrene concentration will cause the polymer cross-linking density to decrease, resulting in the pore size becoming over sized and unstable (Figure 4B). This in turn will lead to the pore walls collapsing or entangling to form a smaller pore size. On the other hand, increasing the DEGDM concentration (which has difunctional double bonds) does not reduce cross-linking density; therefore, there is no pore over sizing and no pore collapse. The same phenomena is also observed in PEGDM; when the polyethylene-glycol unit is too large, the pores become over sized (Figure 4C) and collapse. The result of this collapse is that the relative retention of a water–ammonia solution also decreases (Figure 3 and Table I).

One could argue that the improved separation using the ethyleneglycol derivatives may be caused by increased water absorbency as the number of ethyleneglycol units is increased. To test this effect, DEGDM and TEGDM were replaced with BTDM and HMDM. The results indicate that the ethyleneglycol unit gives better separations than the CH_2–CH_2 unit, as shown in Figure 3. This may be caused by the effect of the water soluble ethyleneglycol units.

The chromatograms shown in Figures 5 and 6 demonstrate that water–ammonia is clearly separated within 4 minutes using one of these columns under isothermal conditions and low flow rate. The PLOT column made from DVB and styrene copolymer is capable of separating water–ammonia solutions and water–HCN solutions (Figure 6). Since water, ammonia, and HCN are present in comets that will be studied in future NASA missions, the DVB–styrene copolymer PLOT column was selected for further study.

Conclusion

Several DVB copolymer and dimethacrylate homopolymer PLOT columns were developed and investigated for the separation of water and ammonia.

Microscopic examination of two PLOT columns made from HMDM in different solvent systems revealed that a suitable solvent system is important for proper polymerization. The sol-

vent system must allow the polymers to form into appropriately sized particles that uniformly coat the column wall.

Using an in situ polymerization method, several DVB copolymer and dimethacrylate homopolymer PLOT columns were developed and investigated for the separation of water and ammonia. Based on the following results, we concluded that the pore size of the polymers plays an important role in the separation of water–ammonia solutions:

- An increase of styrene or EGDM contained in the DVB copolymer increases the relative retention time of water and ammonia
- An increase in the chain length between dimethacrylate functional groups of the dimethacrylate homopolymers also increases the separation between water and ammonia

In addition, because ethyleneglycol chains between dimethacrylate functional groups in the dimethacrylate homopolymer (e.g., TEGDM homopolymer) give better separation than ethylene chains between dimethacrylate functional groups in the dimethacrylate homopolymers (e.g., HMDM homopolymer), the polarity of the polymers also affects water and ammonia separation.
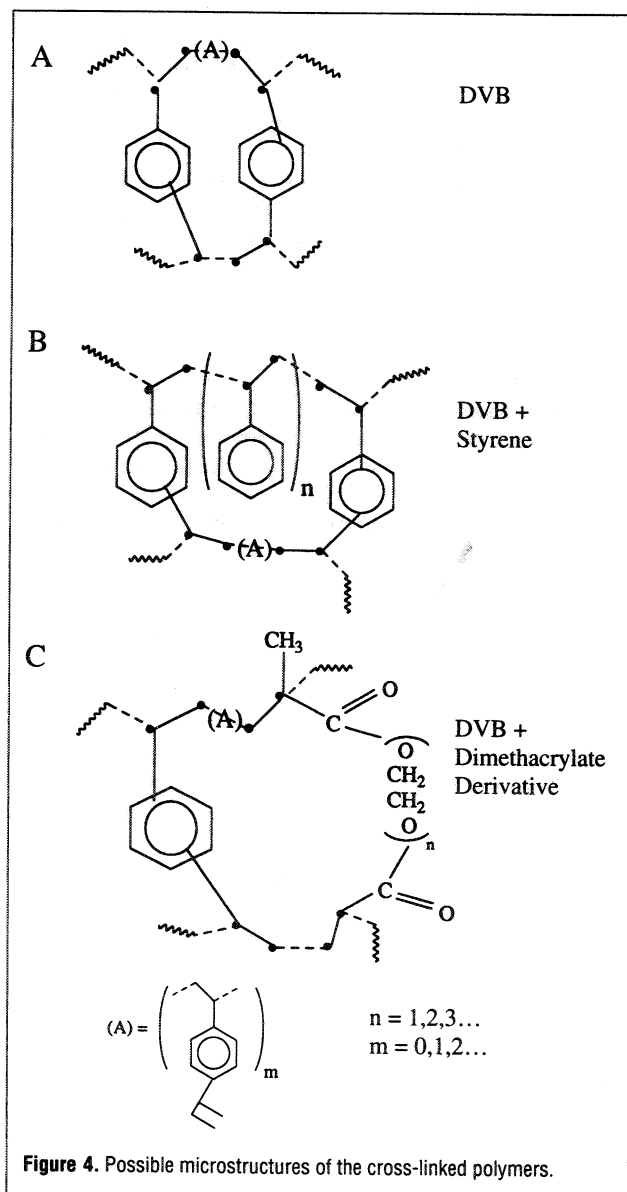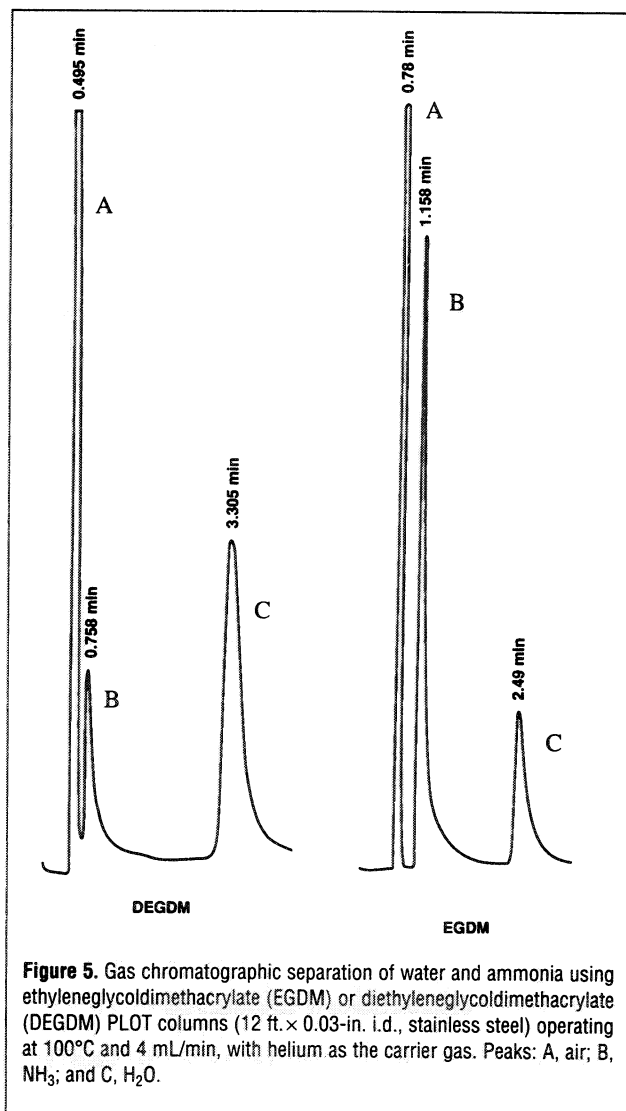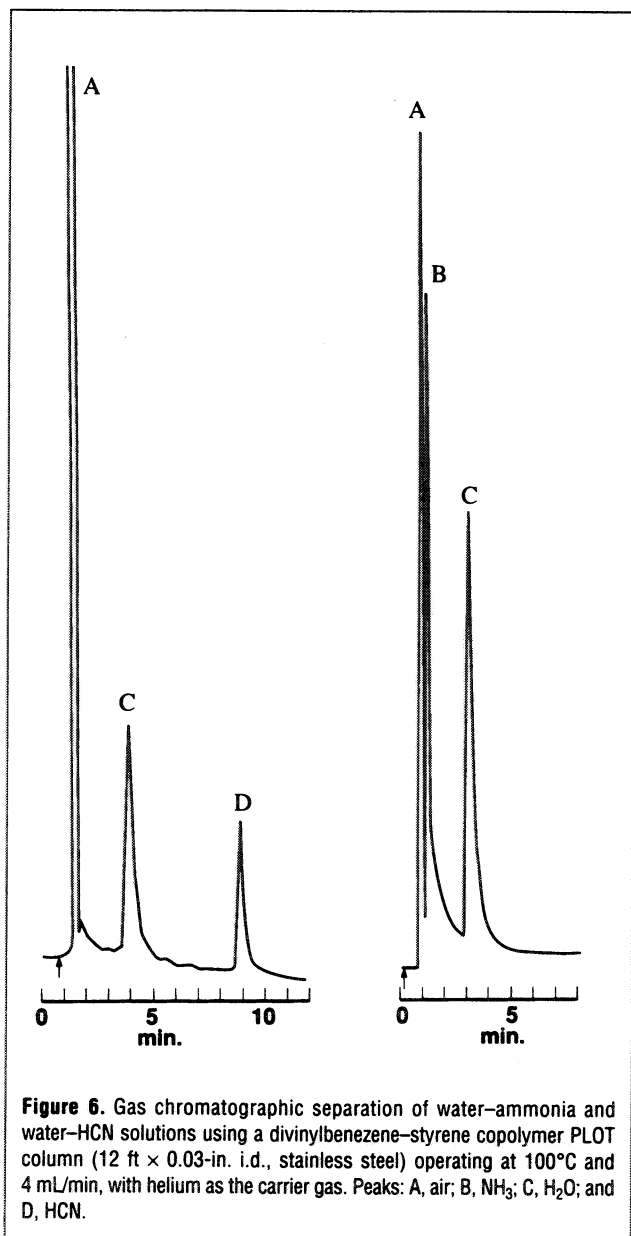
Acknowledgments

Appendix

Key to abbreviations

BTDM	1,4-butanediol dimethacrylate
DEGDM	diethyleneglycoldimethacrylate
DVB	divinylbenzene
EGDM	ethyleneglycoldimethacrylate
HMDM	1,6-hexamethylene dimethacrylate
PEGDM	polyethyleneglycol (400)dimethacrylate
PLOT	porous layer open tubular
PTAA	pentaerythritol triacrylate
PTMA	pentaerythritol tetramethacrylate
TEGDM	triethyleneglycoldimethacrylate
TTEGDM	tetraethyleneglycoldimethacrylate

Figure 4. Possible microstructures of the cross-linked polymers.

Figure 5. Gas chromatographic separation of water and ammonia using ethyleneglycoldimethacrylate (EGDM) or diethyleneglycoldimethacrylate (DEGDM) PLOT columns (12 ft. × 0.03-in. i.d., stainless steel) operating at 100°C and 4 mL/min, with helium as the carrier gas. Peaks: A, air; B, NH_3; and C, H_2O.

Figure 6. Gas chromatographic separation of water–ammonia and water–HCN solutions using a divinylbenzene–styrene copolymer PLOT column (12 ft × 0.03-in. i.d., stainless steel) operating at 100°C and 4 mL/min, with helium as the carrier gas. Peaks: A, air; B, NH_3; C, H_2O; and D, HCN.

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